A model for discrimination freshness of shrimp

Linong Du a, Chunxiang Chai b,⁎, Meijuan Guo c, Xiaoxiang Lu b

a College of Communication Engineering, Tianjin University of Commerce, Tianjin 300134, China
b College of Biotechnology and Food Science, Tianjin University of Commerce, Tianjin 300134, China
c Hebei Food Inspection and Research Institute, Shijiazhuang 050091, China

A R T I C L E   I N F O

Article history:
Received 20 April 2015
Received in revised form 31 October 2015
Accepted 4 November 2015

Keywords:
Electronic nose
Shrimp
Discriminant model
Freshness

A B S T R A C T

The shrimp is popular for its nutrition and dainty, however, it is easy to decay, and its freshness degrades so, it is important to assess its freshness. The shrimp gives off unpleasant odor with its freshness change, detecting its odor difference can evaluate its freshness. The feasibility of using electronic nose for evaluating the freshness of shrimp (Penaeus vannamei) is explored in this paper. The odor of shrimp, stored at 5 °C, was detected by the electronic nose. Combined with the sensory evaluation and TVBN, a model based on the electronic nose was constructed to evaluate the shrimp freshness. In principal components analysis, the first three principal components accounted for 86.97% of total variation, and they are used to establish a model to estimate the shrimp freshness with Fisher Liner Discriminant. The discriminant rates were 98.3% for 120 modeling sample data, and 91.7% for 36 testing sample data. The model could be easily used to evaluate the freshness of shrimp with better accuracy.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Due to its high nutritional value and distinctive flavor with a tender and delicate texture, the consumer demand for shrimp is enormous. In USA, the volume of imports of shrimp was about 1120 million pounds in 2013 [1]. In China, the volume of shrimp culture was about 5314 million pounds in 2011 [2]. Shrimp undergoes bacterial contamination and enzymatic activity during transportation and storage [3–10], the ingredients like protein, fat and carbohydrates are decomposed into ammonia, hydrogen sulfide, ethyl mercaptan, aldehydes, aldehyde acids, alcohols, ketones, aldehydes, and carboxylic acid gases [3,6]. These chemical compounds give rise to off-flavors and other unpleasant characteristic [4–7], the freshness of shrimp degrades. Consumption of spoilage shrimp could cause serious health hazards [3,5]. It is important to assess the freshness of shrimp.

The shrimp freshness is often determined by means of sensory analysis, chemical experiments and microbial population evaluation. The disadvantages of sensory analysis are lack of objectiveness and poor reproducibility. Chemical experiments and microbial population evaluation, such as Total Volatile Basic Nitrogen (TVBN) and the microbial population in shrimp are detected to indicate its freshness; however, these two methods are complex procedures, more expense, time-consuming and destructive. Therefore, a simple and nondestructive method is expected to evaluate the shrimp freshness.

The spoilage shrimp gives off unpleasant odors. If the shrimp odor is detected, its freshness could be assessed. A simple, quick technology to inspect food odor is electronic nose. Electronic nose is a simulation of biological functions to identify some simple or complex odor [11,12]. The electronic nose is used as a non-destructive method for food quality detection [13–17], such as classifying stored grain, analyzing water and wastewater, monitoring roasting process, testing freshness of fish and fruit, controlling the manufacture of cheese, sausage, beer, and bread, and detecting bacterial growth in meat and vegetables.

The electronic nose was also used to measure the shrimp freshness [18–22], the result showed that the electronic nose could detect the odor change of shrimp. Most application of electronic nose focused on pattern recognition techniques [19–26]. Principal component analysis (PCA) was a pattern recognition technique which was often used to reduce the dimensionality of a data set while retaining as much information as possible, employed with tin oxide gas sensor arrays [23]. PCA scores was plotted to demonstrate the separation achieved but no classification algorithm was tried [26], it was inconvenience for predicting unknown samples. The purpose of this study is to construct a model to predict freshness of shrimp; firstly, the principal component was obtained, secondly, Fisher Liner Discriminant was employed to establish a model with the principal component above, and then the freshness of shrimp was predicted with the model.

2. Materials and method

2.1. Sample preparation

Fresh shrimps (Penaeus vannamei, 48 to 54 shrimps per kg) were from Farmers’ Market located at JiaNing Road in Tianjin Beichen District, China. These shrimps were killed using crushed ice. Each shrimp was
placed in 40 ml plastic bottle, sealed with lid and kept in a refrigerator (5 °C). Measurements of shrimp were conducted at scheduled time intervals (12 h) during storage. At first, the sample was performed using sensory analysis, then electronic nose measurements, and finally TVBN.

### 2.2. Electronic nose apparatus

The electronic nose contained a chemical sensor array, a signal processing system and a pattern recognition system. The electronic nose was presented in this work (Fig. 1).

Metal oxide semi-conductors (MOS) respond to many volatile compounds such as formaldehyde, benzene, toluene, ketone, carbon monoxide, carbon dioxide, nitrogen dioxide and ammonia, the MOS was used to make arrays for odor measurement [27]. Six tin oxide sensors was used to form the sensor array, namely TGS2600, TGS4161, TGS2620, TGS813, TGS825 and TGS826 (Figaro Engineering Inc.), these sensors had a good response to the different odors produced by the shrimp. Their feature was listed in Table 1.

These sensors were placed uniformly in testing chamber and respectively numbered X1, X2, X3, X4, X5, X6.

These sensors above are sensitive to ambient temperature and humidity. Air filter, air dryer and temperature controller were designed to minimize the effect of temperature and humidity on signal of sensor (Fig. 1). Air filter and dryer made air dry and clean, temperature controller held the temperature constant. The temperature of the air flowing into the testing chamber was 40 °C, the humidity was 5%, and the air flow rate was 150 ml/min in the tube.

The air, filtered and dried, was sent into sample chamber by the air pump, the odor of the sample was brought into the testing chamber. The odors came into contact with sensors, the sensors responded, and the output voltage was collected, delivered into computer, processed and recognized.

### 2.3. Method

#### 2.3.1. Electronic nose sampling procedure

The electronic nose was turned on, preheated for 30 min before test. The shrimp was placed into the sample chamber. Air pump was on; clean air went through sample chamber. The volatile from the sample was sent into the testing chamber. The gaseous compounds were in direct contact with the sensor arrays located in testing chamber, and the voltage of each sensor changed. The voltage of each sensor was collected by the computer. After each experiment, the testing chamber was cleaned with clean air for 300 s.

#### 2.3.2. Sensory evaluation

The sensory evaluation of shrimp was conducted with a descriptive method [28]. It was performed by a trained sensory panel. The trained sensory panel was composed of ten tasters. All tasters were trained and familiar with sensory evaluation procedure of shrimp. Each shrimp sample was evaluated by ten tasters, according to color, viscosity, elasticity and flavor of shrimp. The mean of the 10 tasters was considered as the score of the shrimp.

#### 2.3.3. Total volatile basic nitrogen (TVBN) evaluation

TVBN evaluation of the shrimp samples was performed using standard protocols [29], the TVBN contents were tested with semimicro Kjeldahl method, and showed as mg per 100 g of shrimp.

### 3. Results

#### 3.1. Sensory evaluation

The sensory evaluation result was shown in Fig. 2. The sensory scores of shrimp decreased as the storage time increased. In the first 2 days, the total score curve only declined slightly, the sensory score changed from 15 to 13, this manifested that the shrimp samples have not corrupted until the second day. 2 days later, the color, viscosity, elasticity and flavor of shrimp changed, and the sensory score declined fast. 4 days later, the sensory score was below 10, the shrimp deteriorated with unpleasant odors and the shrimp was inedible.

![Fig. 1. Electronic nose schematic diagram.](image-url)
3.2. TVBN result

The content of TVBN in shrimp, stored at 5 °C, was detected. The result was listed in Table 2. The TVBN content increased with storage time. It increased fast, from 4.93 mg/100 g to 15.05 mg/100 g when the shrimp was stored for 2.5 days at 5 °C, reached 30.74 mg/100 g at the fifth day, exceeded 30 mg/100 g which was the criterion in standard protocols (GB2733-2005), at this moment, the shrimp went rotten with uncomfortable odor, inflexible tissue and blackening, it was inedible. The generation of TVBN was a complex biochemistry procedure.

3.3. Electronic nose results

3.3.1. Output voltage performance of each gas sensor

According to scheduled scheme, the odor of shrimp was detected using electronic nose. Obtained was the relationship between output voltage of each gas sensor and acquisition time. A preliminary observation of the sensor responses showed that each sensor had an initial voltage \( V_0 \) when clean air flowed past sensor array, a voltage \( V_t \) when the odor of shrimp through sensor array, so the output of each sensor was expressed as relative variation \( (V_t - V_0) \). Each sample was measured for 5 min, a data was collected every 10 s, and 30 data were obtained.

Fig. 3 showed the relationship between output voltage of gas sensor 3 and acquisition time, the shrimp was kept at 5 °C for 2 days. In the beginning, the output voltage increased with acquisition time, it was named rising stage, 2 min later, the output voltage was stable, and it was called stable stage. The stable output voltage of each gas sensor was indicated as the odor of sample, the mean of the stable stage was used as output voltage of each gas sensor. The output signal of other sensors was similar.

3.3.2. The principal component analysis

The sensor array consisted of 6 gas sensors, so every sample had 6 data, these data were expressed as vector \( X = (X_1, X_2, X_3, X_4, X_5, X_6) \). The odor of 156 different fresh shrimp, stored at 5 °C for different time, was detected using electronic nose. 156 different fresh shrimp were classified according to its sensory evaluation and content of TVBN into two groups, fresh shrimp and stale shrimp. The number of fresh shrimp was 78, and the stale shrimp was 78. 120 data (60 fresh and 60 stale) were randomly selected from 156 data to establish model to predict the freshness of shrimp, another data (18 fresh and 18 stale) was used in testing the model. The TVBN value was from 4.93 mg/100 g to 31.23 mg/100 g in the calibration set, 5.32 mg/100 g to 27.42 mg/100 g in the testing set.

PCA was employed to analyze the 120 data using Matlab soft, the principal component characteristic value and contribution were shown in Table 3. Table 3 showed that the three characteristic values of Principal Component were respectively 2.532, 1.709 and 0.978; the accumulative contribution rate was 87%. The three Principal Components explained

![Fig. 2. Sensory evaluation result of shrimp stored at 5 °C.](image)

<table>
<thead>
<tr>
<th>Storage time/day</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>1.5</th>
<th>2</th>
<th>2.5</th>
<th>3</th>
<th>3.5</th>
<th>4</th>
<th>4.5</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>TVBN value</td>
<td>4.93 ± 0.12</td>
<td>9.18 ± 0.10</td>
<td>12.88 ± 0.08</td>
<td>13.59 ± 0.16</td>
<td>14.03 ± 0.14</td>
<td>15.05 ± 0.09</td>
<td>17.48 ± 0.13</td>
<td>19.27 ± 0.06</td>
<td>22.39 ± 0.21</td>
<td>26.17 ± 0.15</td>
<td>30.74 ± 0.12</td>
</tr>
</tbody>
</table>
when $y_0$ the above formula, obtaining $y_0$. When $y_0<0$, this sample was staled. One sample was misjudged in 60 stale samples, and the discriminant rate was 98.3%.

The above formula was tested with 36 testing data along with the formula, obtaining $y_0$. When $y_0<0$, this sample was staled. One sample was misjudged in 60 stale samples, and the discriminant rate was 98.3%.

The above formula was tested with 36 testing data along with the formula, obtaining $y_0$. When $y_0<0$, this sample was staled. One sample was misjudged in 60 stale samples, and the discriminant rate was 98.3%.

### 3.3.3. Discriminant model for the shrimp freshness

A model was established to predict the freshness of shrimp, with the three principal component scores $F_1, F_2$ and $F_3$, using Fisher Liner Discriminant (Matlab soft), the discriminant model was as follows.

$$y_0 = 1.308F_1 - 1.234F_2 + 0.254F_3$$

The three principal component scores of each sample were put into the above formula, obtaining $y_0$. When $y_0>0$, this sample was fresh, and when $y_0<0$, this sample was staled. One sample was misjudged in 60 fresh samples, one sample was misjudged in 60 stale samples, and the discriminant rate was 98.3%.

The above formula was tested with 36 testing data along with the same way. The discriminant rate was 91.7%.

### 4. Discussions

The aim of the study was to seek a technology to assess the freshness of shrimp. The electronic nose was the best choice for its nondestructive, fast and economic. The sensor was selected to form sensor arrays based on their sensitivity to odors of shrimp. The temperature and humidity of the air through the sensor arrays were controlled during measurement.

The output voltage of 6 gas sensors were analyzed using PCA and the three Principal Components were obtained. Fisher Liner Discriminant was employed to establish a model to predict the freshness of shrimp; the sensory evaluation and the content of TVBN were performed to indicate the freshness of the shrimp.

Sensory scores showed decline with storage time, it was consistent with sensory evaluation, which was obtained from appearance, odors, and texture of shrimp, for frozen shrimp performed by Theoefania Tsironi et al. [4]. It showed that shrimp was unacceptable after storage for 4 day, however, it was for 5 day, shrimp stored at 4 °C reported by Tang et al. [19]. It was not performed by Li et al. [20].

TVBN value, shrimp stored at 5 °C for 1 day, was 12.88 mg/100 g, it was similar to the TVBN value 12.19 mg/100 g, stored at 4 °C for 1 day reported by Ash Hocao [9]. It was 22.39 mg/100 g after storage for 4 day, lower than 31.25 mg/100 g performed by Li et al. [20], close to 24.82 mg/100 g reported by Tang et al. [19], shrimp stored at 4 °C. After storage for 5 days, it was 30.74 mg/100 g, exceeding acceptable limits (National Standard of the People's Republic of China, GB2733-2005, 2005).

PCA was often used while electronic nose evaluating the shrimp freshness. PCA scores were plotted to show the separate effect of different shrimp. Tang et al. [19] reported that the odor of shrimp, stored at 4 °C for 6 days, was detected by PEN3 electronic nose, the freshness of shrimp was classified to 3 grading according to sensory evaluation and TVBN value, and The 3 grading was better discriminated in PCA scores scheme. Zhao et al. [21] reported that the odor of head and flesh of shrimp, stored at 0 °C for 10 day, was respectively detected by PEN3 electronic nose, PCA scores scheme showed that the odor of shrimp, storage for different time, was distinguished. Similar result was reported by Li et al. [20]. Chai et al. [18] also reported that the odor of shrimp, respectively stored at 4 °C for 5 days, −10 °C for 20 days, and −15 °C for 60 days was detected by self-made electronic nose, the feature of output signal was extracted, and the effect of storage temperature and time on the feature extracted was studied. These PCA score schemes demonstrated that the separation achieved was inconvenient for predicting unknown freshness of shrimp.

In this paper, the temperature and humidity were controlled to minimize the effect of temperature and humidity on signal of sensor.

![Fig. 3. The output voltage of sensor 3 with change of acquisition time, shrimp stored at 5 °C for 2 days.](image)
during measurement, this was not mentioned in these reports [19–22]. The PCA was used to reduce the dimensionality, three principal component scores were obtained and used to build a model to predict the freshness of shrimp with Fisher Liner Discriminant. The result was better, and the discriminant rates were 98.3% for 120 modeling sample data, and 91.7% for 36 testing sample data. This model was conveniently applied to estimate the shrimp freshness.

5. Conclusions

The sensory evaluation and the content of TVBN were performed to indicate the freshness of the shrimp. Sensory scores showed decline with storage time, and the shrimp was unacceptable after storage for 4 days. TVBN value increased with storage time. When the shrimp was stored for 5 days later at 5 °C, it was 30.74 mg/100 g, exceeding acceptable limits (National Standard of the People’s Republic of China, GB2733-2005, 2005), and the shrimp was rotten and inedible.

The odor of different fresh shrimp was detected using electronic nose, the output of voltage of each sensor increased with acquisition time in the beginning, then got stable 2 min later. The mean of the stable stage was indicated as output voltage of each gas sensor and used to analyze the odor change of shrimp.

The electronic nose consisted of six sensors; six values were obtained to show the odor of shrimp. PCA was employed to diminish the variables, and three principal components were obtained and employed to build a model to predict the freshness of shrimp with Fisher Liner Discriminant. The discriminant rates were 98.3% for 120 modeling sample data, and 91.7% for 36 testing sample data.

Acknowledgments

This work was supported by the Key Project of Science and Technology Foundations of Tianjin Province of China (Grant No. 11JCZDJC17800) and Projects in the National Science & Technology Pillar Program during the Eleventh Five-year Plan Period (Grant No.2012BAD38B01).

References


